PROTOCOL

Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Groundwater Quality and Remediation Progress at DoD Sites

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ABBREVIATIONS AND ACRONYMS

BTEX	Benzene, toluene, ethylbenzene, and xylenes
COC	Contaminant of concern
DMLS	Dialysis multi-level sampler
DNAPL	Dense non-aqueous phase liquid
DoD	Department of Defense
GC-MS	Gas chromatography-mass spectrometry
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
ICP-MS	Inductively coupled plasma – mass spectrometry
LRL	Laboratory reporting level
LDPE	Low-density polyethylene
LNAPL	Light non-aqueous phase liquid
MDL	Minimum detection limit
MNA	Monitored natural attenuation
MTBE	Methyl tertiary-butyl ether
NAES	Naval Air Engineering Station
NAWC	Naval Air Warfare Center
NBVC	Naval Base Venture County
NFESC	Naval Facilities Engineering Service Center
NTU	Nephelometric Turbidity Units
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PDB	Polyethylene diffusion bag
PVC	Polyvinyl chloride
QA/QC	Quality assurance/quality control
RC	regenerated-cellulose
RCDM	Regenerated-cellulose Dialysis Membrane
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	Volatile organic compound

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EXECUTIVE SUMMARY

This protocol report provides guidance and procedures for successfully using regenerated-cellulose dialysis membrane samplers (dialysis samplers). Development of the protocol was funded under project ER-0313 by the Environmental Security Technology Certification Program (ESTCP). The objectives of this protocol report or user's guide are (1) to discuss the principle of operation of membrane diffusion samplers, (2) to present the basic design and steps in construction of dialysis samplers, (3) to discuss the considerations that must be taken into account before deciding to use a dialysis sampler, (4) to present the steps that must be taken in properly deploying, retrieving, and sampling a dialysis sampler, (5) to discuss the interpretation of field results obtained with dialysis samplers compared to other sampling methodologies, and to discuss how results may vary depending on the hydrologic and chemical variation over a well screen or open interval, and (6) to discuss QA/QC samples that should be collected when using dialysis samplers. This report is primarily concerned with the use of dialysis samplers for collection of groundwater samples from wells, but also discusses briefly the use of dialysis samplers for collection of pore water samples from stream or lake sediments. Findings from a number of recent field comparison case studies in which regenerated cellulose dialysis membrane sampler results are compared to other sampling techniques are reviewed.

Dialysis samplers were developed to sample ground water for inorganic and organic constituents using a diffusion-type sampler. The dialysis sampler consists of a tube of high-grade regenerated-cellulose dialysis membrane filled with deionized water and placed inside an outer protective layer of polyethylene mesh. Dialysis samplers must be deployed in the screened or open interval of a well where ground water is flowing past the sampler to obtain a valid sample. Once deployed, the dialysis sampler is left in the well for sufficient time for the concentrations inside the membrane to come to equilibrium with the concentrations of chemical constituents present in the ground water outside the membrane. After the appropriate equilibration time, the dialysis sampler is retrieved from the well and samples are collected in conventional sample containers and shipped to the laboratory for analysis by standard analytical procedures.

Dialysis samplers can collect valid groundwater samples for most inorganic and organic constituents and compare favorably to samples collected by low-flow purging and other conventional purging methodologies. The length of time dialysis samplers should be deployed in the well prior to recovery depends on the equilibration time for the chemical constituents of interest and the time required for restabilization of the groundwater flow field through the open interval of the well. Laboratory equilibration testing and field comparison data suggest that one to two week deployment times are sufficient to sample for most inorganic and organic constituents.

A dialysis sampler should be deployed at the depth where the highest mass flux of the chemical of concern passes through the screened or open interval of each well. This means the variation in groundwater flow and any stratification of concentrations of chemicals of interest should be determined over the length of the screened or open interval prior to the first deployment of a dialysis sampler. For open intervals 5 feet or greater in length, chemical and vertical profiling should be conducted. Chemical profiling may be done by equilibrating dialysis samplers at

closely spaced intervals (every 2 to 5 ft) over the length of the open interval of a well and analyzing them for a parameter indicative of the contamination. Hydraulic profiling may be done using a borehole flow meter or straddle-packer pump setup. Once the deployment depth has been determined dialysis samplers can easily be deployed by one person and sampled by two persons. The basic considerations in deploying diffusion samplers include that they must be installed and remain submerged below the air/water interface in a well and be allowed to equilibrate for the appropriate period of time for the chemicals of concern at a site.

The size of a dialysis sampler should be the shortest of the following lengths depending on the individual well: five feet in length, the length of the well screen, the length of the zone of highest mass influx of the contaminants of concern, or the length that will contain the minimum amount of water needed for the chemicals being analyzed. Deoxygenated deionized water should be used to fill and store dialysis samplers that will be deployed in anoxic wells to avoid altering the concentrations of redox active chemicals. Dialysis samplers made with regenerated-cellulose dialysis membrane must be kept hydrated between the time of construction and deployment. Dialysis sampler limitations due to water volume loss with time and biodegradation are minimized when deployment times in wells are one to two weeks.

Side-by-side comparisons of dialysis samplers with other sampling technologies may be necessary to establish the applicability of dialysis samplers with regulators on a site-by-site basis. It is essential that all parties involved in the use of dialysis samplers at regulated sites must identify and agree on the objectives of data collection, data evaluation techniques, and data end uses before dialysis sampler deployment takes place. No regulatory issues have been identified that would restrict the application of dialysis samplers in technically appropriate situations.

1.0 INTRODUCTION

Regenerated-cellulose dialysis membrane diffusion samplers (dialysis samplers) have been developed as an alternative to the current standard method for collecting groundwater samples from wells by low-flow purging (Puls and Barcelona, 1996) or conventional purging. Unlike purging techniques, dialysis samplers do not require monitoring field parameters to stabilization for lengthy periods of time prior to sampling, do not require decontamination between wells, do not produce purge water that must be collected or treated, and do not produce samples that need to be field filtered. By reducing or eliminating these problems, dialysis samplers greatly reduce sampling field time and therefore greatly reduce overall groundwater sampling costs in comparison to purging methods.

Dialysis samplers also were developed as an alternative to polyethylene diffusion bag (PDB) samplers (Vroblesky, 2001a and 2001b). PDB samplers are diffusion-type samplers that efficiently sample wells for most volatile organic compounds (VOC). However, PDB samplers cannot be used to collect samples for inorganic chemical constituents or some very soluble VOC, such as methyl tert-butyl ether (MTBE) or acetone. The regenerated-cellulose dialysis membrane is permeable to inorganic constituents and to all VOC including MTBE and acetone, and even some semi-volatile organics. For these reasons, dialysis samplers offer the potential to sample for most all parameters of interest at typical contamination sites using a diffusion-type sampler.

The objectives of this protocol report or user's guide are (1) to discuss the principle of operation of membrane diffusion samplers, (2) to present the basic design and steps in construction of dialysis samplers, (3) to discuss the considerations that must be taken into account before deciding to use a dialysis sampler, (4) to present the steps that must be taken to properly deploy, retrieve, and sample a dialysis sampler, (5) to discuss the interpretation of field results obtained with dialysis samplers compared to other sampling methodologies, and to discuss how results may vary depending on the hydrologic and chemical variation present in a well screen or open interval, and (6) to discuss quality assurance/quality control (QA/QC) samples that should be collected when using dialysis samplers. This report primarily is concerned with the use of dialysis samplers for collection of groundwater samples from wells, but also briefly discusses the use of dialysis samplers for collection of pore water samples from stream or lake sediments. This report includes findings from a number of recent field comparison case studies in which regenerated-cellulose dialysis membrane diffusion sampler results were compared to other sampling techniques. Though this report specifically covers dialysis samplers, it is similar in organization to the report by Vroblesky (2001a) on PDB samplers.

1.1 Diffusion Principle

Diffusion membrane samplers involve suspending a container made of a semi-permeable membrane filled with high-purity water at a given depth in a well. All these sampling devices operate on the principle that given a sufficient amount of time, dissolved chemical species will diffuse across a semi-permeable membrane according to Fick's Law of Diffusion, until concentrations inside the sampler are equivalent to those in the ground water surrounding the sampler (Figure 1-1). The rate at which equilibrium is attained is determined by a number of

factors, including the magnitude of the concentration gradient across the membrane, the pore size of the membrane, the size of the chemical species, the temperature of the water, and the hydrophobic/hydrophilic nature of both the chemical species and the membrane. Once the diffusion sampler has reached equilibrium, it is then brought to the surface and the enclosed water sample is transferred to sample bottles for transport and analysis at a laboratory.

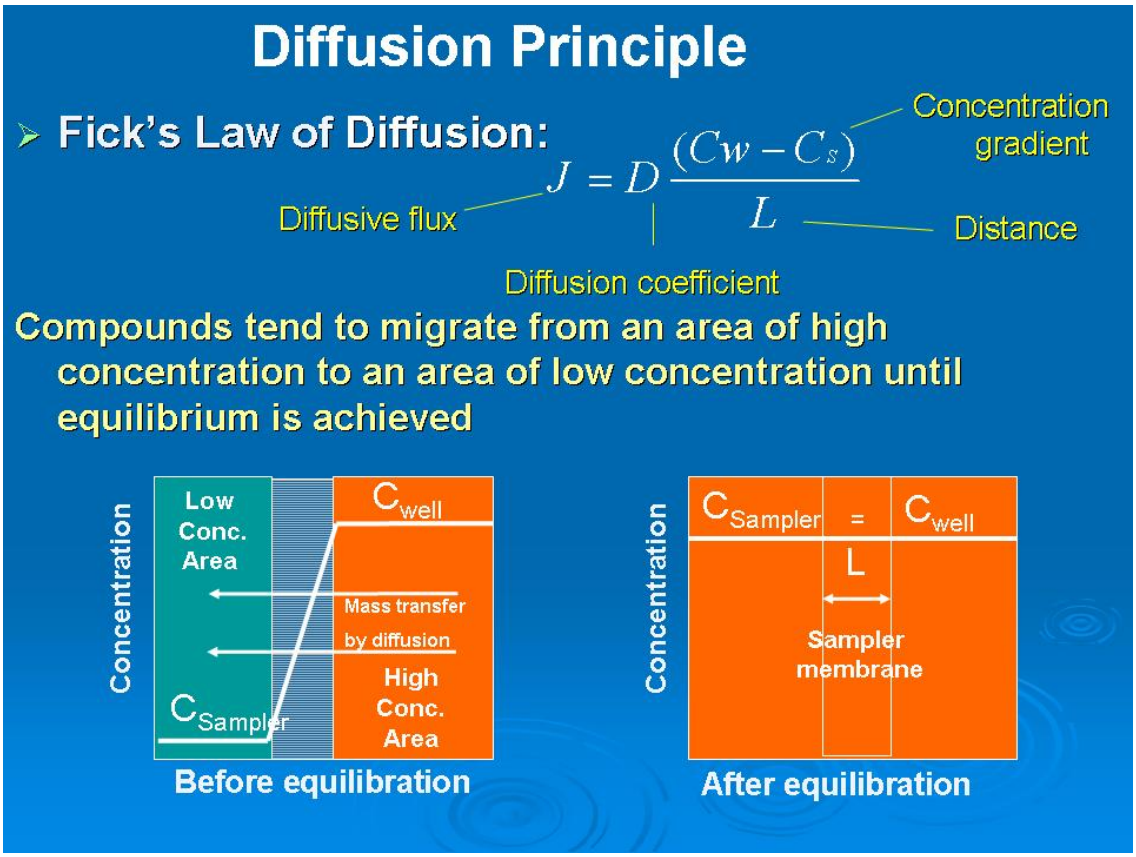

Figure 1-1. Diffusion across a membrane (Fick's Law of Diffusion**) (**Modified from ITRC, 2002**)**

Most diffusion samplers are constructed of low-cost disposable materials that have sufficiently small pores to prevent the passage of suspended particulates into the sampler. If designed properly, essentially no sampling-derived waste water is produced when a well is sampled with a diffusion sampler. Diffusion samplers are quickly and easily installed by one person and recovered and sampled by two persons. Because of their design and operation, diffusion samplers reduce groundwater sampling field time, equipment decontamination costs, and purge-water treatment costs, and avoid the potential extraneous results caused by turbidity in wells.

1.2 Background of Dialysis Sampler Development

Currently, the standard technique for groundwater collection is the U.S. Environmental Protection Agency's (USEPA) low-flow purging procedure using a variable-speed submersible pump with disposable discharge tubing (Puls and Barcelona, 1996). The low-flow technique requires a monitoring well to be pumped at low-flow rates (~500 milliliters per minute (mL/min)) while field parameters are monitored to stability. Often it can take a long period of time (0.75 to 1.5 hours) to reach stabilization before samples can be collected. Following sample collection, time and effort must be spent decontaminating the pump and its components before it can be used in another well to prevent cross-contamination. Contaminated purge and wash water must be collected and transported to treatment facilities for proper disposal. An additional problem in collecting groundwater samples with portable pumps or bailers is that the installation and removal of these sampling devices frequently results in increased turbidity in the ground water brought to the surface. Low-flow purging techniques require that turbidity be monitored until it is less than 10 Nephelometric Turbidity Units (NTU) or becomes stable prior to sample collection. If turbidity is stable but exceeds 5-10 NTU, significant bias can result for many contaminants that sorb readily onto suspended particulates (Gibs et al., 2000). This bias introduces uncertainty into the assessment of inorganic and organic contaminant concentrations in ground water and can result in incorrect conclusions concerning the water-quality or remediation status of a site.

As an alternative to well purging methodologies, several diffusion samplers have been developed over the past two decades, with each having its own advantages and limitations. One design for a diffusion sampler consists of a series of short open-ended rigid polypropylene cylinders with hydrophilic cellulose acetate flat filter membranes covering each end (Ronen et al., 1987; Magaritz et al., 1989). The main advantage of this cellulose membrane diffusion sampler was that it could collect samples for both inorganic and organic chemicals. However, its limitations included a high initial construction cost, the need to decontaminate the sampler between wells, the very small sample volumes it could collect at each depth (20 milliliters [mLs]), and the fact that it could not be used in 2-inch diameter wells. Another diffusion sampler design, the PDB sampler, consists of a tubular-shaped bag made of flexible low-density polyethylene (LDPE) filled with high-purity water (Vroblesky, 2001a, 2001b). PDB sampler advantages include the fact that they are very inexpensive to purchase or construct and can be constructed from small-diameter LDPE tubing that allows them to fit into 2-inch diameter wells. The primary limitation of PDB samplers is that the hydrophobic nature of the LDPE membrane only allows collection of VOC (such as, chlorinated solvents and benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds). The PDB sampler cannot be used to collect inorganic contaminants (such as, trace metals or other dissolved ionic species), inorganic parameters useful for monitored natural attenuation (such as, nitrate, iron, sulfate, or alkalinity), highly soluble organic compounds (such as, MTBE or acetone), or most semi-volatile organic compounds (such as, explosive compounds, polychlorinated biphenyls and polycyclic aromatic hydrocarbons) (ITRC, 2004).

The dialysis sampler discussed in this report is similar to the PDB sampler, but the membrane is made from commercially available tubular regenerated-cellulose dialysis membrane. It has recently been developed by researchers at the U.S. Geological Survey (USGS) (Imbrigiotta et al., 2002; Ehlke et al., 2004; Vroblesky et al., 2002; Vroblesky and Pravecek, 2002; Vroblesky et al., 2003) and at the University of California at Davis (Harter and Talozi, 2004). The main

advantage of the dialysis sampler is that its hydrophilic dialysis membrane allows the passage of both dissolved inorganic and organic contaminants from ground water into the sampler (Imbrigiotta et al., 2007). The regenerated-cellulose dialysis membrane tubing can be purchased in a variety of diameters so the sampler can be made to fit in 2-inch diameter and greater monitoring wells. Dialysis samplers can be made in various lengths to allow for the collection of a sufficient volume of water necessary for the analyses of interest. Dialysis samplers are relatively inexpensive, costing only slightly more than PDB samplers, and are disposable (Imbrigiotta et al., 2007). Table 1 summarizes the advantages and limitations of dialysis samplers.

Table 1-1. Dialysis Sampler Advantages and Limitations.

Advantages
Dialysis samplers can be used to collect samples for analysis for a wide variety of both organic and inorganic chemical constituents in ground water including, anions, silica, methane, dissolved organic carbon, and all VOC (including MTBE), most cations and trace elements, and most explosive compounds.
Dialysis samplers are relatively inexpensive and easy to construct.
Dialysis samplers are easy to deploy, recover, and sample.
Dialysis membranes exclude particulates from groundwater samples, due to their 0.0018-micron pore size; therefore, no field filtration is required.
Dialysis samplers are disposable so there is no need for field decontamination and no potential cross-contamination between wells.
Dialysis samplers essentially eliminate the production of purge water, and hence the need to collect, transport, and treat purge water, when sampling a well.
Dialysis samplers reduce field sampling time and, therefore, significantly reduce the cost of sampling compared to low-flow purging.
Dialysis samplers can be used to vertically profile the chemistry of ground water in the open interval of a well.
Dialysis samplers are particularly advantageous in sampling wells in areas remote from a power source, in high traffic areas, and where a low profile is desirable.
Limitations
Dialysis samplers require two trips to the field, one to deploy and one to retrieve and sample.
Dialysis samplers collect a finite sample volume limited by the diameter and length of the sampler.
Unless the open interval of a well is 5 feet or less, chemical and hydraulic vertical profiling of the open interval is usually needed to determine the deployment depth prior to the first use of a dialysis sampler.
Dialysis samplers must be kept immersed in deionized water between the time of construction and the time of deployment to preserve the permeability, flexibility, and strength of the membrane.
Regenerated-cellulose dialysis membranes are bioactive and do biodegrade with time in groundwater systems. Membranes can be compromised in 4 to 6 weeks in wells; 3 to 4 weeks when buried in stream or lake sediments. Bioactivity on the surface of the membrane may potentially create conditions that allow the transformation of some compounds before they pass through the membrane. These problems are usually not significant because deployment times are typically 1 to 2 weeks for most organic and inorganic constituents.
Dialysis membrane samplers lose a small percentage of their water volume with time (<3%/wk) due to the nature of the dialysis process. Because ideal deployment times are typically 1 to 2 weeks, this usually is not a significant problem in most wells. In wells with higher ionic strength ground water, the rate of volume loss can increase and a rigid mesh support can be inserted into the membrane to limit this loss of volume.

2.0 SAMPLER DESIGN AND CONSTRUCTION

2.1 Basic Sampler Design

The dialysis sampler consists of a deionized water-filled tube of high-grade regenerated-cellulose dialysis membrane inside an outer protective layer of LDPE mesh (Figure 2-1). The sampler may have protective PVC supports external to the dialysis membrane in low-ionic strength waters or an internal perforated PVC pipe or rigid LDPE mesh to support the membrane in higher ionic strength waters. The sampler has a valve at one end to facilitate sample transfer. Each dialysis sampler has an attached or enclosed weight to overcome its buoyancy and is suspended in a well by means of a dedicated or disposable line.

Figure 2-1. Regenerated-Cellulose dialysis membrane sampler (2.5 inches in diameter by 24 inches long**)**

2.2 Regenerated-Cellulose Dialysis Membrane Availability

Fully constructed dialysis samplers are not currently available from any commercial vendors, but must be constructed from easily obtainable components. Regenerated-cellulose dialysis membrane material can be ordered from the vendors listed below:

Membrane Filtration Products, Inc
314 N. River Street
Seguin, Texas 78155
(800) 647-5758
(830) 379-9170
Fax: (830) 379-0720
E-mail: mail@membrane-mfpi.com
website: www.membrane-mfpi.com

Spectrum Laboratories, Inc
23022 La Cadena Drive
Laguna Hills, CA 92653
Phone: (949) 581-3500
Fax: (949) 855-6120
Email: customerservice@spectrumlabs.com
Website: www.spectrapor.com

Purchase of pre-cleaned dialysis membrane material is recommended if trace metals and sulfides are to be sampled. Regenerated-cellulose dialysis membrane remains useable for one to two years if kept refrigerated in its preservative solution of ethanol, sodium benzoate, and ethylene diamine tetra-acetic acid (EDTA). Alternatively, the membrane can be purchased dry, but then must be cleaned in a series of steps that includes soaking and rinsing in deionized water, heated sodium bicarbonate solution, EDTA, and sodium azide solution to remove residual gylcerol, sulfide, cadmium, chromium, copper, iron, nickel, zinc, and lead (Don Keil, Membrane Filtration Products, Inc., written communication, 2002). The pre-cleaned dialysis membrane costs slightly more than the dry membrane but more than makes up the difference in preparation time saved.

The regenerated-cellulose dialysis membrane used to construct dialysis samplers has an average pore size of 18 Angstroms and a molecular weight cut-off of 8000 Daltons. The membrane can be purchased in 50-mm and 100-mm flat widths. Table 2-1 gives the filled diameters and volumes per centimeter and foot of these two most commonly used widths which are used to construct samplers for 2- and 4-inch diameter wells.

Table 2-1. Dialysis Membrane Widths, Filled Diameters, and Filled Volumes.

Well Diameter	Lay-flat Width	Filled Diameter		Filled Volume	
(inches)	(mm)	(mm)	(inches)	(mL/cm)	(mL/ft)
2	50	31.8	1.25	7.94	242
4	100	63.7	2.50	31.87	971

Therefore, for example, dialysis samplers made to fit in 2-inch and 4-inch diameter wells that are 63 cm (24.8 in) long will contain volumes of 500 mL and 2008 mL, respectively.

2.3 Sampler Construction

Because ready-made dialysis samplers cannot currently be purchased commercially, the materials must be purchased and the samplers constructed prior to their use in the field. Sampler construction should take place in clean conditions (e.g., in a laboratory or another controlled environment). The user should wear clean disposable gloves while assembling the sampler to avoid contamination during assembly. It is important to have a source of high-quality deionized water available when assembling, filling, and storing dialysis samplers. The fill water must be free of the chemicals of interest that are in the wells at the target contamination site.

2.4 Sampler Assembly

The pre-cleaned regenerated-cellulose membrane is first cut into lengths long enough to enclose the volume of water that will be needed for all analyses at a particular well. The membrane is then rinsed thoroughly with high-quality deionized water to remove the preservative solution in which it is shipped. The rinsed membrane is then tied in a knot or clamped to close one end and clamped to a clean disposable PVC valve at the opposite end (Figure 2-2). A length of protective LDPE mesh is cut slightly longer than the membrane. For samplers that will be used to sample low ionic strength waters, PVC supports are installed into the ends of the mesh external to the dialysis membrane (Figure 2-3). The mesh protects the dialysis membrane from abrasion against the well casing and screen during deployment and retrieval and the external PVC supports relieve pressure from the mesh on the ends of the dialysis membrane. The membrane with attached valve is then slipped inside the protective mesh and supports. Weights sealed in LDPE bags are installed in the end of the sampler opposite the sampling valve and the mesh is closed with a cable tie. Approximately 450 grams (1 pound) of weight is sufficient to overcome the buoyancy of a 63 to 91 cm (2 to 3 ft) long sampler. Alternatively, plastic-coated or stainless-steel weights can be attached external to the mesh in the field prior to use. The dialysis membrane is filled with high-quality deionized water through the valve. Once filled, the valve is closed, and the mesh is closed at that end using a cable tie also. This encloses the dialysis membrane inside the protective mesh (Figure 2-4).

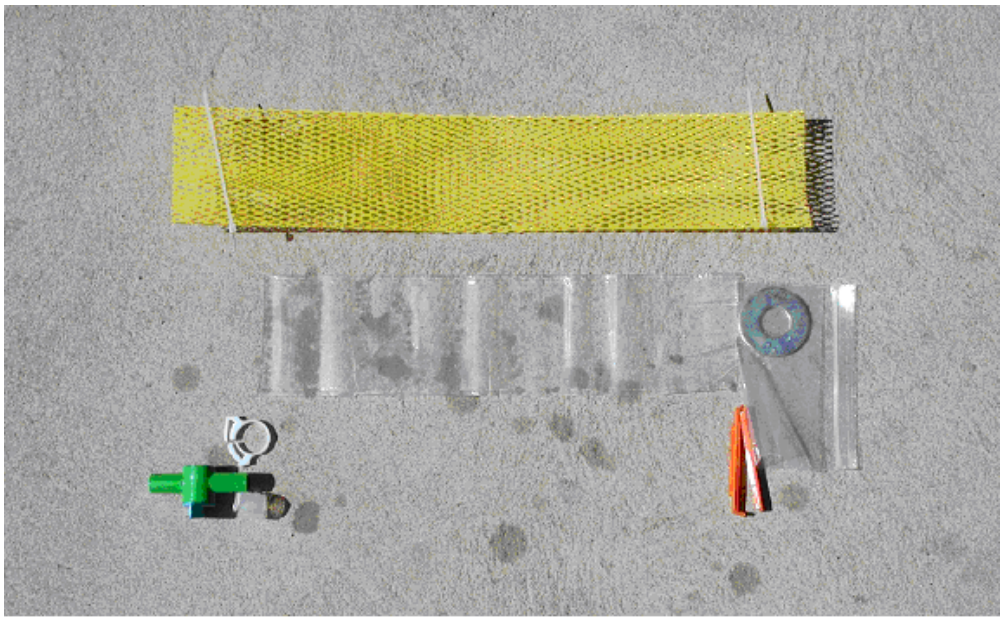

Figure 2-2. Component parts of a regenerated-cellulose dialysis membrane sampler before assembly.

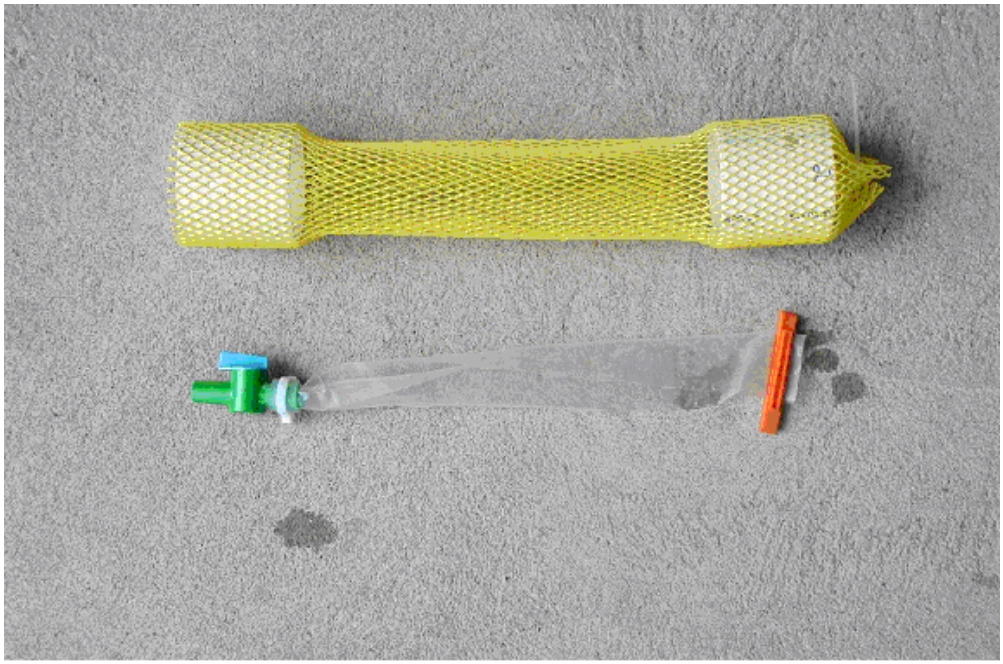

Figure 2-3. Partially assembled Regenerated-Cellulose dialysis membrane sampler before filling with deionized water with external supports installed in the protective mesh.

Figure 2-4. Fully assembled Regenerated-Cellulose dialysis membrane sampler with supports external to the dialysis membrane (2.5 inches in diameter by 15 inches long**)**

For wells with higher ionic strength ground water, a rigid LDPE mesh or perforated PVC pipe can be inserted inside the dialysis membrane before the sampling valve is attached (Vroblesky et al., 2002; Vroblesky and Pravecek, 2002). The internal support ensures that a minimum volume of water will remain in the dialysis sampler. The membrane containing the internal support is then inserted into the protective LDPE mesh without the external PVC supports (Figures 2-5a and 2-5b). This version of the dialysis membrane is filled and enclosed in the protective mesh in the same way as described above.


(a)

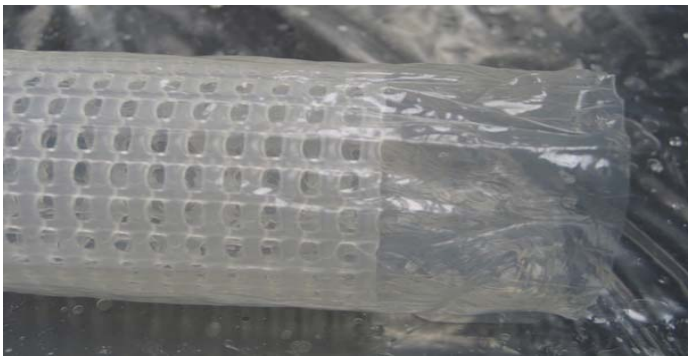
(b)

Figure 2-5. Regenerated-Cellulose dialysis membrane sampler with rigid internal support made of (a) perforated PVC and (b) LDPE mesh.

2.5 Sampler Storage Prior to Deployment

Dialysis samplers should be constructed within a few weeks of deployment and must be kept immersed in deionized water between construction and deployment. If allowed to dry out, the membrane material becomes stiff and brittle and the membrane's diffusive properties may change. The samplers can conveniently be kept wetted by sliding them into a LDPE sleeve knotted at one end, partially filled with deionized water, and then knotted or clamped at the other end. The LDPE sleeving is inexpensive and can be purchased in wall thicknesses strong enough to retain its integrity even when containing water and a dialysis sampler. The sealed LDPE sleeve only needs to be partially filled with water because the headspace in the sleeve will be saturated with water vapor to the extent necessary to keep the membrane hydrated. Alternatively, dialysis samplers can be submerged in a clean plastic bucket or PVC tube filled with deionized water. All these methods of keeping a dialysis sampler hydrated are effective and allow easy transport to the field site.

2.6 Filling Samplers for Anoxic Wells

Dialysis samplers should be filled or equilibrated with deoxygenated deionized water if the sampler is to be deployed in an anoxic well where redox active constituents, such as iron, are to be sampled. Fill water can be deoxygenated by sparging it with nitrogen for at least one hour. Newly constructed samplers can be filled with deoxygenated water and should be stored in deoxygenated water overnight prior to deployment in anoxic wells. Previously constructed samplers can be re-equilibrated in deoxygenated water overnight prior to deployment in anoxic wells.

2.7 Suspension Line

Dialysis samplers are suspended in a well by attachment to a disposable or dedicated line. Polypropylene rope is inexpensive and strong enough to use for this purpose (Figure 2-1). More expensive stainless-steel lines and plastic-coated stainless-steel lines may also be used (Figure 2-6). The suspension line should be measured and marked so the sampler can easily be set at the desired depth in the well. Suspension lines or ropes are attached in the field just before deployment of the sampler in a well.

Figure 2-6. Example of dialysis sampler with a plastic-coated stainless-steel suspension line (2.5 inches in diameter by 36 inches long**).**

3.0 CONSIDERATIONS PRIOR TO USE OF DIALYSIS SAMPLERS

Prior to the use of dialysis samplers several points should be considered to ensure that these samplers are appropriate for collection of water samples in a particular situation. Such considerations as the type of water sample needed, number of trips to the field, well construction, deployment depth, sampler size, contaminants to be sampled, equilibration times, biodegradation, and volume loss must all be taken into account. Based on these evaluations, it is possible in some instances that it may not be appropriate to use a dialysis sampler. Most of these considerations are also applicable to all no-purge sampling devices.

3.1 Use and Application of Dialysis Samplers

The primary use and application of dialysis samplers discussed in this protocol is to collect both inorganic and organic constituents from ground water in wells. Dialysis samplers can be used to vertically profile the concentrations of contaminants over the open interval of a well by suspending multiple samplers at regular intervals. Dialysis samplers can also be used to sample long-term monitoring wells in contaminant plumes by suspending one sampler at a chosen depth. Dialysis samplers have been successfully used to monitor wells for a wide variety of both organic and inorganic chemical constituents by a number of researchers (Tunks et al., 2000; Vroblesky et al., 2002; Vroblesky and Pravecek, 2002; Imbrigiotta et al., 2002; Vroblesky et al., 2003; Harter and Talozi, 2004; Parsons, 2005; Imbrigiotta et al., 2007). A secondary application of dialysis samplers is to collect pore water samples from stream and lake sediments. Dialysis samplers buried in stream or lake sediments have been somewhat successful when used to determine areas of groundwater input of contamination by trace metals and explosive compounds to surface water (G. Nicholas, NJDEP, written communication, 2000; LeBlanc, 2003).

Dialysis samplers should only be used to collect dissolved constituents from ground water or sediment pore water. Dialysis samplers do not collect whole water samples due to their small pore size. Dialysis samplers should only be used to collect constituents that have been tested and determined to diffuse through the regenerated-cellulose dialysis membrane and equilibrate in a consistent time period. The constituents tested are detailed in Section 3.6 below.

3.2 Trips to the Field

Users must be aware that the use of dialysis samplers requires two trips to the field to collect a sample, one to deploy the samplers and one to retrieve the samplers. This may be problematic depending on the travel distance to the site. Diffusion samplers can easily be deployed by one person and sampled by two persons. However, dialysis samplers should not be left in the well for longer than 4 weeks because of the possibility of biodegradation of the membrane (see section 3.7 below).

3.3 Well Construction

The depth and length of the well screen or open interval of a well must be known and must contain enough water to allow the sampler to remain submerged below the air/water interface in the well over the period of its equilibration. A recent water-level measurement from the well and the response of the water level in a well to nearby pumping are needed to ensure that the dialysis sampler will remain submerged while installed in the well. If the water level declines in a well due to pumping, such that a dialysis sampler is exposed to the air for a portion of the time it is

suspended in a well, the membrane may dry out and crack and sample may not represent the chemistry of the ground water in the well at the time the sampler is recovered.

Practically, wells with inside diameters of two inches or greater can be sampled with dialysis samplers. Regenerated-cellulose dialysis membranes can be purchased in smaller diameters that would fit down smaller diameter wells, but samplers made with these membranes would have severe sample volume limitations. Dialysis samplers have been used to sample wells to depths of 410 ft but there is no obvious reason why the samplers should not be useable in wells at greater depths.

3.4 Deployment Depth and Vertical Profiling

For the dialysis sampler (or any no-purge sampler) to work properly it must be allowed to equilibrate with chemical concentrations in ground water flowing naturally through the open interval of a well. The depth of deployment of a dialysis sampler is therefore crucial to collecting a representative sample. Unless dialysis samplers are being used to vertically profile contamination over the open interval of a well, their depth of deployment should not be arbitrary. The dialysis sampler should be placed at a depth where the highest mass flux of the chemicals of interest passes through the open interval of each well similar to the recommendation for PDB samplers made by the ITRC (2004). This means the variation in groundwater flow and any chemical stratification of dissolved concentrations should be determined over the length of the open interval prior to deployment of a dialysis sampler. Vertical profiling, preferably by both hydraulic and chemical methods, is recommended to obtain this information.

If the open interval of a well is short (<5 feet), vertical profiling is optional. With short open intervals, dialysis samplers can be positioned in the center of the screen. For wells with larger open intervals (>5 feet) vertical profiling should be done to determine the optimal depth for deployment (ITRC, 2004). This entails some extra work prior to the initial time a well is sampled with dialysis samplers. However, this effort need not be repeated before any subsequent sampling events.

Hydraulic vertical profiling in a single borehole is done to determine zones of inflow and outflow in a well's open interval. The profiling typically is accomplished using either a straddle-packer pump setup or a borehole flow meter. The straddle-packer pump method involves packing off and test pumping small sections of the open interval to determine where the zones of higher or lower transmissivity are over the length of the open interval. Although, this procedure works well in uncased fractured-rock wells and in some unconsolidated sand-and-gravel wells where most of the groundwater flow through the open interval is horizontal, the results of pumping from straddle packers in screened wells are only qualitative because of the potential for flow through the sand pack. Borehole flow meters allow measurement of horizontal or vertical flow in a well. A common type of vertical flowmeter is a heat-pulse flow meter. Typically, vertical flow is measured under static and pumped conditions to determine predominant zones of inflow and outflow. As with the straddle-packer pump approach, the heat-pulse flowmeter works well in uncased fractured rock boreholes but can only be used in a qualitative manner in screened wells. If the lithology of an unconsolidated formation that the screened interval intercepts is known and fairly uniform (for example, sand and gravel), horizontal flow through the screened interval is likely also relatively uniform.

Chemical vertical profiling can be accomplished by equilibrating, sampling, and analyzing dialysis samplers (or any no-purge samplers) that have been suspended at closely spaced intervals (every 2 to 5 ft) over the length of the screened or open interval of a well. Vertical profile samples only need to be analyzed for one or two parameters that are indicative of the contamination present at a site. The purpose of the profiling is to determine the zones of highest concentration of a target contaminant. Chemical vertical profiling works only when vertical mixing due to diffusion or advection is limited.

In addition to hydraulic and chemical vertical profiling information, some knowledge of the site geology, lithology, and past contamination history is also required to make an informed decision on the depth of deployment. For example, given a well with a long screen that intersects the water table, a site with light non-aqueous phase liquid (LNAPL) fuel contamination would be expected to have higher concentrations shallower in the well, whereas, a site with (DNAPL) chlorinated solvent contamination would be expected to have higher concentrations deeper in the well.

Based on all this information, the dialysis sampler usually should be positioned at the depth of the zone of highest mass flux of the contaminant of concern. That is, the depth at which the groundwater flow times concentration gives the highest mass per time. Deployment at this depth should allow the collection of ground water from the open interval of a well that will be most representative of ground water from the aquifer.

3.5 Sampler Volume and Length

The maximum volume that a dialysis sampler should contain is that enclosed in a 5-ft long sampler of the diameter that will fit down the well casing. This is in keeping with the desire to have a diffusion sampler not represent more than 5 ft of an open interval (ITRC, 2004). The volumes enclosed by dialysis samplers constructed to fit down 2-inch and 4-inch wells can be calculated based on the length and the information given in Table 2-1. The maximum length of a diffusion sampler should never be longer than the open interval of a well itself or the length of the zone of highest mass flux present in the open interval. Dialysis samplers as long as 4.5 feet have been constructed, deployed, and sampled successfully. As a matter of practicality, dialysis samplers that are greater than 3 feet in length become somewhat unwieldy and are difficult to manipulate. In longer samplers there is also a concern that different chemical concentrations may be sampled by the top and bottom of the sampler if chemical stratification is present over the sampled interval.

The volume of water contained in a diffusion sampler can be adjusted by varying the length and diameter of the membrane used in its construction. Once constructed, the volume of the sampler is finite. For this reason, it is important to carefully determine the minimum volume of water needed for all the chemical analyses that will be run on a sample before sampler construction begins. Discussion of analytical minimum volume requirements with the laboratory often can lead to reductions in the total volume of water needed. This minimum volume should be increased by 10-20% to allow for water used to rinse bottles or losses during sample transfer in the field. Planning for a small amount of extra water volume in the diffusion sampler may result in a small volume of water that must be disposed; however, if the volume is too small, the

problem may involve sacrificing certain analyses because minimum volume requirements cannot be met.

3.6 Analyte Permeability and Equilibration Times

The chemical constituents of interest in a well must be able to diffuse through the dialysis membrane and reach equilibrium within a reasonable time to be effectively sampled by a dialysis sampler. Analyte permeability and equilibration times have been determined for a large number of both organic and inorganic chemicals in laboratory studies. Ehlke et al., (2004) tested the permeability of the regenerated-cellulose dialysis membrane for iron, bromide and six chlorinated VOC in the laboratory at 21°C. They found that iron and bromide equilibrated within 3 to 7 days and the six chlorinated VOC equilibrated within 1 to 3 days. Vroblesky et al., (2002) lab tested the permeability of the dialysis membrane and determined equilibration times for arsenic, chloride, chromium, iron, lead, manganese, selenium, and sulfate at room temperature. All of these inorganic constituents equilibrated within 1 to 4 days. Harter and Talozi (2004) tested the equilibration times for nitrate and specific conductance in dialysis samplers and found both equilibrated within 1 day.

Imbrigiotta et al., (2007) tested the permeability of dialysis membrane for 59 VOC, major cations and anions, trace elements, dissolved organic carbon, methane, and sulfide and determined equilibration times for these constituents. These tests were done at two temperatures (10°C and 21°C) and at two different concentrations. Test results showed that lower water temperatures caused slightly slower equilibration for some constituents than at higher temperatures due to decreased diffusion rates. Test results also showed that some elements or compounds equilibrated slightly faster when higher concentrations were present in the test ground water than when lower concentrations were present in the test ground water due to the increased concentration gradient. Results at all temperatures and concentrations showed equilibration within 1 to 3 days for anions, silica, methane, sulfide, dissolved organic carbon, and all VOC on the USEPA 8260b list (including MTBE) and 3 to 7 days for most cations and trace elements. Mercury, silver, and tin were the only trace elements that did not equilibrate within 28 days.

Equilibration times for selected explosive compounds through dialysis membranes were determined by LeBlanc (2003). These tests were run at 4°C and revealed that HMX and RDX were 75-80% equilibrated after 12 days. More recently Parker and Mulherin (2006) conducted laboratory equilibration tests for HMX, 1,3,5-trinitrobenzene, RDX, and TNT at room temperature and found these explosive compounds equilibrated in dialysis samplers within 7 to 14 days.

Table 3-1 summarizes all the chemical constituents that have been permeability and equilibration time tested in laboratory studies for dialysis samplers. The table gives the range of equilibration times in parentheses next to the name of each group of compounds.

Table 3-1. Analytes Tested in the Laboratory for Permeability and Equilibration Times Through Regenerated-Cellulose Dialysis Membranes.

Constituents reaching 95% equilibration or greater in dialysis samplers in 1 to 14 days (number of days to equilibration indicated in parentheses)		
VOC (1-3 days)		
1,1,1,2-Tetrachloroethane	2,2-Dichloropropane	Isopropylbenzene
1,1,1-Trichloroethane	2-Chlorotoluene	m-Xylene
1,1,2,2-Tetrachloroethane	4-Chlorotoluene	Methyl tert-butyl ether
1,1,2-Trichloroethane	Benzene	Methylene chloride
1,1-Dichloroethane	Bromobenzene	n-Butylbenzene
1,1-Dichloroethene	Bromochloromethane	n-Propylbenzene
1,1-Dichloropropene	Bromodichloromethane	Naphthalene
1,2,3-Trichlorobenzene	Bromoform	o-Xylene
1,2,3-Trichloropropane	Bromomethane	p-Isopropyltoluene
1,2,4-Trichlorobenzene	Carbon tetrachloride	p-Xylene
1,2,4-Trimethylbenzene	Chlorobenzene	sec-Butylbenzene
1,2-Dibromo-3-chloropropane	Chloroethane	Styrene
1,2-Dibromoethane	Chloroform	tert-Butylbenzene
1,2-Dichlorobenzene	Chloromethane	Tetrachloroethene
1,2-Dichloroethane	cis-1,2-Dichloroethene	Toluene
1,2-Dichloropropane	Dibromochloromethane	trans-1,2-Dichlroethene
1,3,5-Trimethylbenzene	Dibromomethane	Trichloroethene
1,3-Dichlorobenzene	Dichlorodifluoromethane	Trichlorofluoromethane
1,3-Dichloropropane	Ethylbenzene	Vinyl chloride
1,4-Dichlorobenzene	Hexachlorobutadiene	
Cations and Trace Metals (3-7 days)		
Calcium	Barium	Molybdenum
Magnesium	Cadmium	Nickel
Potassium	Chromium	Selenium
Sodium	Copper	Vanadium
Aluminum	Iron	Zinc
Arsenic	Lead	
Antimony	Manganese	
Anions (1-3 days)		
Bicarbonate/Alkalinity	Chloride	Sulfate
Carbonate/Alkalinity	Fluoride	Nitrate
Bromide		
Explosives (7-14 days)		
HMX	TNT	1,3-TNB
RDX		
Other Parameters (1-3 days)		
Silica	Methane	Specific conductance
Dissolved organic carbon	Sulfide	
Constituents reaching 95% equilibrium or greater in dialysis samplers in 28 days or more.		
Trace elements (greater than 28 days)		
Mercury	Silver	Tin

3.7 Biodegradation of Dialysis Membrane

Several previous studies of dialysis samplers noted that regenerated-cellulose dialysis membranes became discolored or biofouled during extended equilibration periods ranging from 2 to 3 weeks in shallow wells with warm groundwater temperatures (~21^{o}C) (Vroblesky and Pravecek, 2002; Vroblesky et al., 2003). The concern of these authors was that the discoloration of the membrane was an indication that biodegradation of the dialysis membrane was occurring. They felt if the membrane was biodegrading, then there was a potential for sample compromise due to loss of sampler structural integrity or due to transformation or degradation of the target contaminants resulting from interaction with the microbially active surface of the membrane.

In using dialysis samplers in sediment pore water investigations, researchers have noted the physical breakdown of cellulose membranes when buried in sediment for extended periods (Hopner, 1981; Martens and Klump, 1980). Leblanc (2003) suspected that bacterial action on dialysis samplers buried in lake-bottom sediments contributed to making the membranes brittle and easily breakable. Many samplers in that study were broken prior to sample recovery which the author attributed to biodegradation effects. The study allowed dialysis samplers to equilibrate with the pore water of lake sediments for 2 to 3 weeks.

Imbrigiotta et al., (2007) compared biodegradation of four identical dialysis samplers in a well at the NAWC West Trenton, New Jersey site. The samplers were removed and weighed at approximately one week intervals, and then redeployed in the same well. The average groundwater temperature during this test was ~15^{o}C. Discoloration was noted after one week but did not appear to become any more severe with time. The first perforations were observed in one sampler after 4 weeks. The other three samplers developed perforations over the course of the next two weeks. The authors concluded that dialysis samplers should retain their structural integrity for at least 4 weeks in a well at ~15^{o}C before biodegradation would compromise the membrane. These findings imply that biodegradation should not be a significant structural integrity limitation for dialysis samplers over deployments of one- to two-weeks, which was sufficient time for all the constituents measured in their report. The problems experienced in the previously mentioned studies may have been the result of their longer deployment times, warmer groundwater temperatures, and proximity to high bacterial populations in lake sediments.

The possibility that bioactivity on the surface of the regenerated-cellulose dialysis membrane may produce localized redox conditions that are more reducing than in the ground water in the rest of the well has been suggested (Vroblesky et al., 2003); D. Vroblesky, USGS, written communication, 2006). If such conditions exist, they may allow degradation or transformation of some degradable compounds (e.g., VOC) or redox sensitive chemicals (e.g., iron) as they pass through the membrane. This mechanism has not been confirmed in the field and needs further investigation.

3.8 Volume Loss Due to Dialysis Process

The process of diffusion through the regenerated-cellulose dialysis membrane occurs in both directions simultaneously. At the same time the dissolved ions in well water are diffusing inward to equilibrate inside the sampler, the deionized water is slowly diffusing outward, essentially to try and dilute the aquifer to deionized water. Previous studies had pointed out this loss of sampler volume during the equilibration period in wells with high ionic strength ground

waters (Vroblesky et al., 2002; Vroblesky and Pravecek, 2002). The volume lost was determined in these studies to be severe enough to warrant the insertion of a rigid support inside the regenerated-cellulose membrane to limit the reduction of the sampler volume.

Imbrigiotta et al., (2007) used dialysis samplers to sample wells in the coastal plain and bedrock aquifers of New Jersey where dissolved solids concentrations were relatively low (<500 mg/L) and to sample wells in the coastal plain aquifer at Port Hueneme, California near the Pacific Ocean where total dissolved solids (TDS) concentrations were much higher (up to 2300 mg/L). All dialysis samplers were constructed without internal rigid supports and were weighed prior to deployment. Samplers were re-weighed in the field immediately after retrieval from a well. The weight differences for 28 different dialysis samplers showed an average volume loss of 2.7% per week. The volume loss only in the high dissolved solids wells at the Port Hueneme site ranged from 0 to 7% per week. From these findings, it was concluded that the volume loss due to dialysis appeared to be small even for wells with dissolved solids concentrations as high as 2,300 mg/L. The <3% volume loss per week was not considered a limitation for dialysis samplers, since one to two week deployment periods were sufficient for most constituents measured.

4.0 SAMPLER DEPLOYMENT, RECOVERY, SAMPLE COLLECTION

Once it has been determined that dialysis samplers are appropriate for use in collecting samples from a well, the next step is to deploy them properly. Typically, the weighted dialysis sampler is lowered on a dedicated line to the chosen depth and secured at land surface. Dialysis samplers must be allowed to equilibrate for the appropriate length of time for the constituents of interest. After equilibration, the dialysis sampler is removed from the well, the outside protective mesh is cut back, and water is drained from the device using the sampling valve into conventional sample bottles.

4.1 Transporting Samplers to the Field

Dialysis samplers made in the laboratory must be transported to the field in containers filled with water to keep the dialysis membrane hydrated. If the field site is remote from the laboratory or it will be several days before the dialysis samplers can be deployed, samplers in LDPE sleeves containing water can be shipped to the field site in coolers on ice. The cooler temperatures will retard any possible bacterial growth relative to shipping at ambient air temperatures. Dialysis samplers should not be allowed to freeze during shipment because this may cause the membrane to rupture.

4.2 Initial Well Measurements

The depth to water, the total depth of the well, and the depth of the open or screened interval must be known or determined prior to the installation of the dialysis samplers. This will ensure that the chosen depth of the dialysis sampler is submerged below the water level in the well and is located within the screened or open interval of the well.

4.3 Installation

Sampling personnel should wear clean disposable gloves when installing dialysis samplers. Sharp objects or tools that could puncture the dialysis membrane should be avoided. The dialysis sampler is attached to the previously measured suspension line at the appropriate depth using cable ties or stainless-steel clips. The line is either attached through the mesh or through holes in the external supports. The sampler is then simply lowered slowly into the well. Once submerged in the water column, the dialysis sampler should easily sink to the desired depth if it includes sufficient weight to overcome its buoyancy. The suspension line must be secured to the casing at land surface during the period of deployment. The installation of a dialysis sampler is easily accomplished by one person.

4.4 Deployment Period

Dialysis samplers must be deployed in a well for the length of time necessary for (1) the chemicals of interest to come to equilibrium inside the sampler and (2) for the well to return to hydraulic equilibrium. The equilibration times for those chemicals that have been tested in the laboratory have previously been given in Table 3-1. Removal of the dialysis samplers from a well before chemical equilibration is completed may result in the collection of lower chemical concentrations than those actually present in the well. Depending on the transmissivity of the aquifer formation and the construction of the well, hydraulic restabilization times can vary from a few hours to several weeks. Unless a well is in a tight formation, in most cases the restabilization time will take place in less than 2 weeks.

4.5 Sampler Recovery and Sample Collection

In the field, after the appropriate deployment period, the dialysis sampler is retrieved by pulling up the suspension line. Once the sampler is at the surface, observations as to the weight of the sampler, any significant reduction in the volume of the sampler, the appearance of the sampler, the presence of any perforations in the membrane, or the presence of biological growth on the membrane should be made prior to collection of the samples.

To collect a water sample from the dialysis sampler, it may be convenient to suspend it on a hook on the door of the field vehicle with the sampling-valve end pointing downward. Alternatively, one person simply can hold the sampler up so the sampling-valve end is pointing downward. The protective mesh is cut away from the lower end to allow access to the sampling valve. The valve is rinsed out with deionized water to remove any particulates that may have collected in it while suspended in the well. An extension tube is inserted into the sampling valve to help prevent splashing and direct the flow of water from the sampler. Samples are collected by opening the sampling valve and collecting the water from the sampler in conventional sample containers. Use of the sampling valve allows easy and quick transfer of the sample while minimizing its exposure to atmosphere. If the sampler is not equipped with a sampling valve, the membrane must be opened by unclipping one end or cutting one end and pouring the sample carefully into the sample containers. Dialysis samplers should be sampled as soon as possible after removal from the well and with as little aeration or physical disturbance of the water as possible to minimize any potential loss of volatile compounds or change in redox active chemical species. Dialysis sampler recovery and sampling is easily accomplished by two persons. Users should wear disposable gloves when recovering and handling the sampler and collecting water samples.

4.6 Disposal and Decontamination

If the dialysis sampler is sized correctly for the number and type of sample bottles being filled, all water from the sampler should be collected in the bottles. Thus, at sites where the ground water is contaminated and must be treated as a hazardous waste, the use of dialysis samplers can essentially eliminate the need to collect, transport, and treat purge water from the well. If water is left over in the dialysis sampler after all sample bottles have been filled, the volume should be small (milliliters) and can be disposed of by the procedures established in the site safety plan. Used dialysis samplers, including the dialysis membrane, the protective mesh, the sampling valve, and the clamp, can all be discarded after the samples are collected. At hazardous waste sites, the parts of the sampler as well as any gloves worn during sampling should also be disposed of as hazardous waste by procedures established in the site safety plan. The rigid supports and suspension line can either be discarded or retained and dedicated to that well for use in future sampling events. If kept, these parts should be dried and stored in a labeled polyethylene bag. The weights used may be retained and cleaned so they can be reused in subsequent samplings.

5.0 DATA INTERPRETATION

Before the water-quality results produced by any new sampling technique are accepted by regulators, they usually must be compared to results produced by a widely accepted sampling method in a side-by-side comparison. If the results compare favorably, the new sampling technique is then considered validated. Dialysis samplers have been tested in a number of field comparison studies against low-flow purging because for the last decade low-flow purging has been the USEPA standard method recommended for sampling wells (Puls and Barcelona, 1996). The results of these field comparison studies are summarized in this section.

These studies have used a variety of different tools, including graphical and statistical techniques, to compare the data collected with dialysis samplers with data collected by low-flow purging and other sampling methods. Examples of these tools are discussed in this section.

It is important to determine why the results obtained with dialysis samplers sometimes disagree with low-flow purging or other sampling methods. Explanation of the differences can help understand situations where dialysis samplers should and perhaps should not be used. The effects of vertical chemical stratification and hydraulic heterogeneities over the length of the well screen or open interval are especially important is this regard. These effects are discussed in this section also.

5.1 Tools Used in Data Comparisons

In most cases studies, the interpretation of the data comparisons is made using one or more graphical or statistical comparisons. The choice of which of these interpretive tools is used depends on the specific circumstances and objectives of each study. The primary graphical tool used to compare sets of data collected by two different sampling techniques for one constituent is the 1:1 correspondence plot. This is a scatter plot of pairs of data produced from the same well at the same depth by two different sampling techniques. Ideally, if both sampling techniques recover equal concentrations of a chemical constituent, the data points on a plot will fall on a 1:1 line passing through the origin. The amount of deviation from the 1:1 line can easily be seen on such a graph. When comparing data over several orders of magnitude in concentration, log scales can be used. Examples of 1:1 plots of dialysis sampler results and low-flow purging results for manganese (a cation) and chloride (an anion) from Imbrigiotta et al., (2007) are shown in Figures 5-1 and 5-2 below.

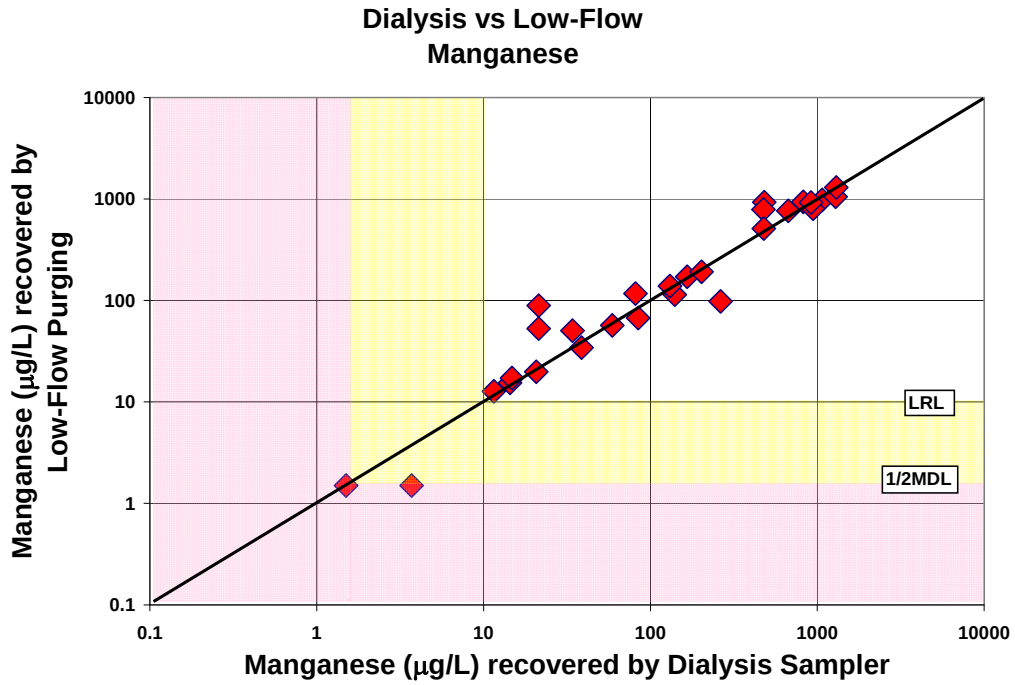

Figure 5-1. Example of a 1:1 correspondence plot of dialysis sampler verse low-flow purging results for manganese (from Imbrigiotta et al., 2007**) (**LRL, lower reporting limit; ½ MDL, one half minimum detection limit; □g/L, micrograms per liter**)**

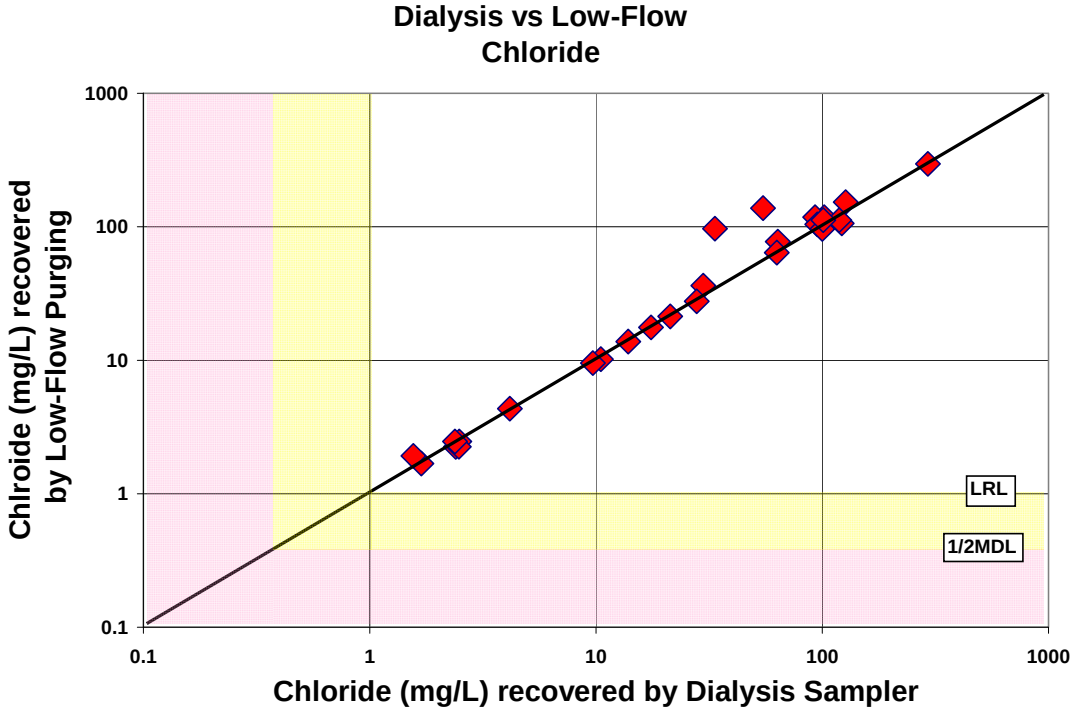

Figure 5-2. Example of a 1:1 correspondence plot of dialysis sampler verse low-flow purging results for chloride (from Imbrigiotta et al., 2007**) (**LRL, lower reporting limit; ½ MDL, one half minimum detection limit; mg/L, milligrams per liter**)**

Similar 1:1 plots have been used to compare results by constituent by Vroblesky et al., (2003), Harter and Talozi (2004), Parsons (2005), and Imbrigiotta et al., (2007). Parsons (2005) has also used these graphs to plot groups of data (for example, all VOC or all trace metals) produced by different samplers. This tactic allows the presentation of a great deal of data on one graph but necessarily obscures the comparisons for individual parameters.

Another less often used graphical comparison is the use of bar charts with parallel bars representing the concentration of a constituent recovered by each sampler in each well. If the bars are equal or close in height, then the samplers are recovering nearly equal concentrations. The drawback to this presentation is that only a finite number of wells can be displayed on one page. Imbrigiotta et al., (2002) and Vroblesky et al., (2002) used bar charts to present data comparisons.

A variety of statistical analyses can also be used to compare the results from different sampling techniques. Some studies have used relative percent difference calculations. In cases such as this, if the difference between concentrations produced by different sampling techniques at the same depth in the same well is smaller than some pre-agreed upon percentage, the samplers are deemed to agree and the sampler is validated. Dialysis samplers were compared to low-flow purging and PDB samplers using this technique by Vroblesky and Pravecek (2002).

Simple correlation analysis can be done between sets of data produced by two different sampling techniques. If the two samplers recover approximately equal results over a range of concentrations, then the correlation coefficient (r) between the two sets of data should be highly positive. However, other distributions of data pairs can also give highly positive correlations and not be a linear relationship over all concentration ranges. Therefore, the conclusion that sampling techniques are recovering the same concentrations should not be based solely on a correlation analysis.

Use of least-squares regression analysis may also be used to compare sets of concentrations recovered by two different sampling techniques. Ideally, if both sampling methods recover identical concentrations of a constituent, the least-squares regression line through the data comparison points should have a slope of 1 and an intercept of 0. The difference between the actual slope and intercept from these values can be used as a measure of how well the two sampling methods agree. Parsons (2005) and Imbrigiotta et al., (2007) used this type of analysis to compare sampling techniques.

A more powerful way of determining whether two data distributions are different is to use statistical testing procedures. If the data are normally distributed, parametric tests can be used. A student's t-test is the simplest way to determine if the difference between two sets of results (from two sampling techniques) is significant at a known confidence level (e.g. 95%). If the data are not normally distributed, non-parametric statistics can be used. A Wilcoxon Rank Sum test is equivalent to a non-parametric student's t-test. Non-parametric tests operate on the ranks of the data rather than the actual concentrations recovered. Even so, they usually have very similar power to determine whether a difference between two sets of results is significant at a known confidence level. For more complex comparisons between more than two sampling techniques at a time, a parametric one-way analysis of variance can be used for normally distributed data

and a non-parametric Kruskal-Wallis test or analysis of variance on ranked data can be used for non-normally distributed data. Parsons (2005) and Imbrigiotta et al., (2007) used these statistical techniques when comparing the results of dialysis samplers to several other sampling methods in their studies.

5.2 Field Comparison Case Studies

A variety of field studies have been conducted comparing dialysis samplers to low-flow purging, PDB samplers, and other types of diffusion samplers in their ability to sample for a wide variety of common inorganic constituents and VOC.

Dialysis samplers have been tested and reported on at the following sites: McClellan AFB, California (3 wells) (Parsons, 1999; Tunks et al., 2000), Naval Air Warfare Center, West Trenton, NJ (9 wells) (Imbrigiotta et al., 2002), Naval Industrial Ordnance Plant, Fridley, MN (2 wells) (Vroblesky et al., 2002), Hickam AFB, Hawaii (13 wells) (Vroblesky and Pravecek, 2002), Davis, California (43 wells) (Harter and Talozi, 2004), Massachusetts Military Reservation, Cape Cod, MA, (130 samplers buried in lake sediments) (Leblanc, 2003), Andersen AFB, Guam, (5 wells) (Vroblesky et al., 2003), McClellan AFB, California (20 wells) (Parsons, 2005), and Naval Air Engineering Station, Lakehurst, NJ (6 wells), Naval Base Ventura County, Port Hueneme, CA (8 wells), and Naval Air Warfare Center, West Trenton, NJ (8 wells) (Imbrigiotta et al., 2007).

A field study conducted at McClellan Air Force Base, Sacramento, CA (Parsons, 1999; Tunks et al., 2000) compared the ability of a multi-level dialysis sampler (using cellulose acetate dialysis membranes), a PDB sampler, low-flow purging, and conventional 3-volume purging to sample for chlorinated VOC in three wells. Results obtained from samples collected with all four sampling methods were not significantly different in their recovery of 7 chlorinated VOC.

A field comparison study conducted at the Naval Air Warfare Center, West Trenton, NJ, (Imbrigiotta et al., 2002) sampled 9 wells with dialysis samplers, low-flow purging, and a modified conventional purge method for chlorinated VOC, calcium, chloride, iron, and alkalinity. The dialysis sampler results compared very favorably (no statistical difference at the 95% confidence level) with the purging techniques for all these constituents.

Dialysis samplers were compared to low-flow purging and nylon screen samplers in a field comparison study at the Naval Industrial Reserve Ordnance Plant, Fridley, MN, (Vroblesky et al., 2002) in their ability to sample 2 wells for arsenic, calcium, chloride, iron, manganese, and sulfate. Results for all these inorganic constituents obtained with both the dialysis sampler and the nylon screen sampler agreed well with results from low-flow purging in these wells. This report did point out that sampling redox-active constituents, such as iron, was sometimes problematic if anaerobic wells were sampled with nylon-screen samplers filled with aerobic water. Iron concentrations in such cases were frequently overestimated compared to low-flow purge samples. In at least one well, dissolved iron diffusing into the nylon-screen samplers combined with the dissolved oxygen present in the water inside to form an iron oxide precipitate. Vroblesky et al., (2002) reasoned that if the nylon-screen sampler was sampled before the precipitate redissolved, the iron would be included in the sample and result in higher iron concentrations in the diffusion sampler than with low-flow purging. This was confirmed in at

least one well. No precipitation of iron inside any of the dialysis samplers tested in this study was observed, but was postulated as a potential problem for all diffusion membrane samplers in sampling for redox sensitive trace metals.

In another study conducted at Hickam Air Force Base, HI, (Vroblesky and Pravecek, 2002) 13 wells were sampled with dialysis samplers, PDB samplers, and low-flow purging for aromatic VOC, alkalinity, arsenic, chloride, iron, lead, methane, sulfate, sulfide, and zinc. Results compared favorably for VOC samples collected with all three sampling techniques and inorganics collected with the dialysis sampler and low-flow purging.

Harter and Talozi (2004) compared dialysis samplers to conventional purging in 43 wells in sampling for specific conductance and nitrate. Dialysis samplers compared favorably with a conventional 5-10 volume purge technique for these two water-quality parameters.

LeBlanc (2003) buried dialysis samplers in the sediments of a lake near the Massachusetts Military Reservation, Cape Cod, MA in an attempt to determine if explosive compounds in ground water from the base were discharging into the lake. Over 130 dialysis samplers were installed in the lake sediments and allowed to equilibrate for 13 to 27 days before retrieval and sampling. The results were compared with a like number of drive-point pore water samples collected from the pore sediments of the lake adjacent to the locations where the dialysis samplers had been buried. Four explosive compounds were detected at low concentrations in samples from the dialysis samplers. No explosive compounds were detected in samples from the drive-point water samples. Because so few comparisons resulted, no conclusions were made about the applicability of dialysis samplers to sample for explosives in this manner, but clearly the dialysis samplers provided an indication that explosives compounds were present in the lake sediments.

Five wells were sampled for chlorinated VOC and chloride at Andersen Air Force Base, Guam, using dialysis samplers, PDB samplers, nylon screen samplers, and low-flow purging (Vroblesky et al., 2003). Dialysis samplers were found to recover chloride concentrations as well as low-flow purging. However, dialysis samplers were found to generally recover lower TCE and PCE concentrations when compared to both PDB and low-flow purging. The reason for the disagreement was postulated to be due to the fact that the ground water at this study site was very low in oxidizable organic carbon and that the regenerated-cellulose membrane may itself have been used as a carbon source by bacteria in the wells to create localized conditions around the samplers that were more conducive to TCE and PCE biodegradation. In addition, the longer equilibration times (22-23 days) used in this study may have contributed to this phenomenon.

A study comparing a number of different diffusion samplers and purging technologies was conducted in 20 wells at McClellan Air Force Base, Sacramento, CA (Parsons, 2005). Dialysis samplers, PDB samplers, rigid porous polyethylene samplers, polysulfone samplers, a downhole thief sampler, a disposable polyethylene grab sampler, low-flow purging, and conventional purging were all compared in their ability to sample for anions, trace metals, hexavalent chromium, 1, 4-dioxane, and VOC. Results of this study indicated that dialysis samplers recovered concentrations of VOC, anions, 1,4-dioxane, and hexavalent chromium as well or better than low-flow purging. Parsons (2005) noted that dialysis samplers generally recovered

lower concentrations of trace metals than low-flow purging in their comparison tests but did not detail which trace metals were included in the comparison. One possible reason for different concentrations being recovered by dialysis samplers and low-flow purging was that there was a 7 to 10 day lag time between when the samples were collected with each of these sampling techniques due to the experimental design of their study. Additionally, no vertical profiling was done prior to the multi-sampler deployments in the test wells at McClellan AFB, so differences in recovery of metals between diffusion samplers and purging methods may be due to the diffusion samplers not being deployed at the depth of highest mass influx. In addition, they also found dialysis samplers recovered lower concentrations of VOC than PDB samplers to which they were attached. Both the PDB and dialysis samplers had been deployed and recovered at the same time. Again, the authors did not detail which VOC were included in the comparisons. Overall, the dialysis sampler was rated equal in ability to low-flow purging in sampling chemicals in this study.

A study comparing dialysis samplers, to low-flow purging and PDBs was conducted at Lakehurst Naval Air Engineering Station, Lakehurst, NJ, Naval Base Ventura County, Port Hueneme, CA, and Naval Air Warfare Center, West Trenton, NJ (Imbrigiotta et al., 2007). In this study 28 wells were sampled for cations, anions, trace elements, VOC (including MTBE), DOC, sulfide, methane, and TDS. Dialysis samplers and PDB samplers recovered all VOC equally well at all sites. Dialysis sampler results were not statistically significantly different from low-flow purging results for 21 of the 24 VOC detected in wells in this comparison. Only n-butylbenzene, p-isopropyltoluene, and sec-butylbenzene differed significantly between sampling techniques. In all cases, these three compounds were recovered equally by both the dialysis sampler and the PDB sampler and in lower concentrations than low-flow purging. This indicated that both types of diffusion samplers recovered the ambient concentrations of these VOC present in water in the casing prior to low-flow purging. The authors suggested low-flow purging may have drawn higher concentrations of these compounds into the well from a part of the aquifer that does not normally intercept the open interval of the well under non-pumping conditions. Results for 28 of 30 inorganic and selected organic constituents showed concentrations were recovered statistically equally well by dialysis samplers and low-flow purging. Only nickel and sulfide differed significantly. Nickel was found in higher concentrations in low-flow samples compared to dialysis samples, but 10 of 11 comparisons in this study were below the laboratory reporting limit for this trace element. Sulfide was recovered in equal or higher concentrations in dialysis samples than in low-flow samples. The explanation for this finding was not immediately apparent and further study of dialysis samplers for this constituent is needed.

The results for all of the water-quality constituents tested in the above mentioned case studies are summarized in Table 5-1 below. The overwhelming majority of field comparison results shown in Table 5-1 prove that dialysis samplers can collect as valid a sample as a low-flow purging procedure for most of the inorganic and organic constituents tested.

Table 5-1. Water-Quality Parameters Tested in Field Comparison Studies.

Parameters with favorable field comparison results (Case studies concluded dialysis samplers and purging methods showed good agreement.)		
VOC		
1,1,1-Trichloroethane	cis-1,2-Dichloroethene	o-Xylene
1,1-Dichloroethane	Dichlorodifluoromethane	p-Xylene
1,1-Dichloroethene	Ethylbenzene	Styrene
1,2,4-Trimethylbenzene	Isopropylbenzene	tert-Butylbenzene
1,2-Dibromoethane	m-Xylene	Tetrachloroethene
1,3,5-Trimethylbenzene	Methyl tert-butyl ether	Toluene
Benzene	Methylene chloride	trans-1,2-Dichlroethene
Chloroform	n-Propylbenzene	Trichloroethene
Chloromethane	Naphthalene	Vinyl chloride
Cations and Trace Metals		
Calcium	Antimony	Lead
Magnesium	Barium	Manganese
Potassium	Cadmium	Molybdenum
Sodium	Chromium	Selenium
Aluminum	Copper	Vanadium
Arsenic	Iron	Zinc
Anions		
Bicarbonate/Alkalinity	Chloride	Nitrate
Bromide	Fluoride	Sulfate
Explosives		
RDX	HMX	
Other Parameters		
Silica	Ethene	Total dissolved solids
Methane	Carbon dioxide	Specific conductance
Dissolved organic carbon		
Parameters with questionable field comparison results (Case studies could not confirm dialysis samplers and purging methods gave the same results.)		
p-Isopropyltoluene	n-Butylbenzene	sec-Butylbenzene
Nickel	Sulfide	

5.3 Potential Reasons for Differences Between Field Comparison Results

Although dialysis sampler results agreed closely with low-flow purging results in most field comparison studies, in relatively few cases the methods recovered different concentrations. The reasons for the disagreements are important to determine because these situations may lead to a better understanding of where dialysis samplers should and should not be used. Possible reasons may include differences in the design of the field comparison tests, well construction, sampling mechanisms, the acceptance criteria agreed upon with regulators, the vertical and lateral distribution of contamination present, and the vertical variation in lithology and hydrology of the aquifer at a site. It is important to remember, that in most cases, the fact that different concentrations are obtained by the different sampling techniques does not necessarily mean one method is right and the other is wrong. It may mean that the methods are sampling different water from the same well (ITRC, 2004).

5.3.1 Field Comparison Test Design

Field comparison tests should be conducted such that samples collected with the dialysis sampler are obtained as close in time as possible to samples collected with low-flow purging. However, not all tests have been designed this way. Some field comparison tests in the literature have allowed the dialysis sampler to equilibrate and be recovered, then allowed another sampling device to equilibrate and be recovered, before a low-flow purging sample was collected. In some instances the difference in time was 1 to 2 weeks between the time the dialysis sample and the low-flow sample were collected. Concentrations of constituents in ground water can change significantly over this length of time and result in the two sampling techniques obtaining different results. All field comparison sampling with different sampling methods should be conducted as close to one another in time as possible to eliminate this source of variation.

5.3.2 Well Construction

Comparison tests should be set up such that samples from the dialysis sampler and any other sampler type can be collected from the same depth in the well. This can be a problem particularly in small diameter wells where side-by-side comparisons of dialysis samplers with other no-purge sampling devices cannot be done simply because the samplers will not fit in the well screen next to one another. If it is physically impossible to conduct side-by-side comparisons, different sampling devices should be deployed in a well at as close to one another in depth as possible. In these instances, the differing depths of the samplers may introduce some variation in the results if any chemical stratification is present in the screened or open interval of the well.

5.3.3 Sampling Mechanisms

Variation between dialysis samplers and low-flow purging results may occur because of the difference between sampling mechanisms. Diffusion samplers can only equilibrate with water that flows past them during the period of time and at the depth they are suspended in a well. In other words, dialysis samplers collect a point sample from one depth in the open interval. On the other hand, purge pumps draw water in over the entire open or screened interval of a well even at low-flow rates (Britt, 2005; Varlgen et al., 2006). Low-flow purging collects an integrated sample from the entire open interval, not simply a point sample from one depth.

5.3.4 Acceptance Criteria

Variation between dialysis sampler and low-flow purging results can also occur because the criteria for deciding whether they are different may be too rigorous. The criteria to determine if dialysis and low-flow purging results are different should not be set, for example, to a relative percent difference of +/- 15% if it is known that the variation in the laboratory analysis for the compounds of interest is +/- 30%. This will simply result in finding most comparisons to be different when in reality the differences are due to analytical variations.

5.3.5 Chemical Stratification and Hydraulic Heterogeneity

Variation between dialysis sampler and low-flow purging results in comparison studies may also occur because of the presence of chemical stratification and/or hydraulic heterogeneity in the open interval of a well. Vroblesky (2001a) noted that chemical stratification and hydraulic heterogeneities over the depth of the screened or open interval of a well sometimes were important causes for disagreement between the VOC results of PDB samplers and purging methods. Since dialysis samplers and PDB samplers both operate by diffusion mechanisms, it stands to reason these effects will similarly impact comparisons between dialysis samplers and low-flow purging results. In previous studies, significant chemical stratification of VOC has been found to occur over depths as small as 5 to 10 feet in well screens using pumping and passive sampling techniques (Pearsall and Eckhardt, 1987; Gibs et al., 1993; Vroblesky and Peters, 2000). Significant variation has also been found in the amount of ground water input to a well at different depths over a 15- to 20-ft screened interval due to aquifer heterogeneity (Gibs et al., 1993; Reilly and Gibs, 1993).

Ideally, the depth at which comparison testing should be conducted is the depth at which the highest mass flux of the contaminant of interest is entering the well screen or open interval. As previously discussed, in section 3.4, the depth can be determined by vertically profiling the concentrations of an indicator parameter and by vertically profiling the input of ground water using a straddle packer setup or a borehole flow meter. Where the depth with the highest concentration matches up with the depth with the highest ground water input, deploying the samplers in this zone of highest mass influx ensures the highest probability that the dialysis sampler and low-flow purging results will agree. This is the approach used in many of the field comparison case studies discussed in the previous section, and in most of them, the concentrations collected by dialysis samplers and low-flow purging agreed.

In wells where results of dialysis samplers and low-flow purging do not agree, it appears that a combination of the presence of both chemical stratification and hydraulic heterogeneity in the open interval is frequently the cause. Particularly, discrepancies seem to occur when the depth of the highest concentration and the highest groundwater input to the well do not occur at the same depth. An example of such a situation would be a well in which high contaminant concentrations with lower ground water input are found shallow in the open interval and low contaminant concentrations with higher groundwater input is found deeper in the open interval. Depending on the exact concentrations and input flows, the depth of highest mass influx can be either in the shallow or the deep part of the open interval. If the depth of highest mass flux is located at the shallow depth and the dialysis sampler is deployed there, in the absence of vertical flow or in-well mixing, the dialysis sampler will recover the high concentration but the low-flow purging pump, though deployed at the same shallow depth, will move more water from the

deeper depth that is less contaminated and will recover an overall lower concentration. Conversely, if the depth of highest mass flux is located in the deeper portion of the open interval and the dialysis sampler is deployed there, in all likelihood, the dialysis sampler will recover the low concentration, but the low-flow purge pump placed at the same deeper depth, will move some water from the shallower depth that is more contaminated and will recover an overall higher concentration. Therefore, caution should be exercised when evaluating comparison study results from wells where the depth of highest concentration and highest groundwater input do not coincide

Another case where the results of dialysis samplers and low-flow purging have been found to disagree is a well in which below detection contaminant concentrations and very low groundwater input were found during vertical profiling. When the dialysis sampler was deployed at what was thought to be the depth of highest mass flux, no detectable contaminant concentrations were found in the well. However, when the well was low-flow purged from the same depth, concentrations of several hundred micrograms per liter were detected (author's unpublished data from NAWC site). It is believed that the pumping drew the contamination into the well from a source that normally would not have intercepted the open interval. Such a source could be located either laterally or downgradient from the open interval or vertically above or below the open interval. In this instance, though the dialysis sampler and low-flow purging recovered different concentrations, the dialysis sampler probably represents the ground water in the aquifer under ambient (non-purging) conditions more accurately.

6.0 QUALITY ASSURANCE AND QUALITY CONTROL

6.1 Quality Assurance/Quality Control Samples

Quality-control samples should make up 10-20% of the total number of samples analyzed during a site study. Quality-control samples collected for dialysis samplers should include:

- Duplicate dialysis samplers should be deployed in 10% of the wells sampled during a site study. Duplicate dialysis samplers should be suspended side-by-side at identical depths in the open interval of a well if at all possible. If not possible, then the duplicate samplers should be suspended at depths as close together as possible.
- A dialysis sampler equipment blank consists of an extra dialysis sampler that is suspended in deionized water for the same length of time as the samplers are equilibrated in the wells in the field. After the deployment period is up, the diffusion sampler stored in the deionized water is sampled and analyzed identically to those recovered from wells.
- Trip blanks should be analyzed at least for volatile constituents to determine if cross-contamination is occurring between sample containers during storage and shipment.
- A source water blank of the deionized water used to fill the dialysis membrane samplers should be analyzed for all parameters that will be analyzed in the regular samples in the study just to be sure that there is no contamination of any constituent of interest in the source water.

6.2 Potential Sources of Variation Between Replicate Samplers

Some variation in the concentrations of chemicals recovered will inevitably occur between replicate dialysis samplers placed in the same well. The primary potential sources for variation between replicate dialysis sampler results are the use of contaminated construction materials, use of different handling or storage procedures, and use of different deployment or sampling procedures.

6.2.1 Construction Materials

Replicate dialysis sampler results may vary because of potential contamination of the materials used to construct the sampler. To avoid this, all parts used to construct a dialysis sampler should be cleaned identically and thoroughly. All parts used in construction of these samplers should be as chemically non-reactive as possible. Regenerated-cellulose dialysis membranes purchased pre-cleaned from the manufacturer are certified to be free of a variety of contaminants, including trace metals and sulfides, below a specified level (D. Keil, Membrane Filtration Products, written communication, 2002). This was confirmed in the bench-scale equilibration testing conducted by Imbrigiotta et al., (2007) who found no trace metals, sulfides, or VOC desorbing in any of the blank tests of the manufacturer's pre-cleaned dialysis membranes. Equipment blanks analyzed in the field comparison portion of this same study found no leaching of any cations, anions, VOC, or trace metals, except zinc. Since zinc did not come from the regenerated-cellulose dialysis membranes, it was attributed to the use of galvanized washers that were used as weights for the samplers. Use of stainless-steel or plastic-coated weights should alleviate this problem.

6.2.2 Handling and Storage

Dialysis sampler results can vary if different handling and storage procedure are used for different replicate samplers. All dialysis samplers should be handled by personnel wearing

disposable sampling gloves while they are being assembled, transported, installed, recovered, or sampled. If a sampler must be laid down it should be laid on clean plastic sheeting or aluminum foil. Dialysis samplers should be stored identically in deionized water free of the chemicals to be sampled between the time of construction and deployment so the membranes do not dry out, become physically cracked, or alter their diffusive properties.

6.2.3 Deployment and Sampling

Replicate dialysis samplers may vary if not installed or sampled identically. When chemical stratification exists in the open interval of a well (no vertical flow or mixing), short differences in installation depth can potentially expose different samplers to water with significantly different concentrations. To minimize this variation, replicate dialysis samplers should always be installed at the same depth in the open interval of a well as determined by the initial chemical and hydraulic vertical profiling. Suspension lines should be stretched out tightly while being measured to be certain the markings on the line will accurately reflect the true depth of the sampler when it is installed.

Dialysis sampler results may differ if replicate samplers are not allowed to equilibrate for the same length of time. Dialysis samplers should always be deployed for the appropriate amount of time to allow for both hydraulic restabilization to occur in the well and chemical equilibration to occur in the sampler. If one sampler is removed before hydraulic restabilization and chemical equilibration have occurred, the concentration may not match the concentration of a sampler left in for the appropriate length of time.

Results from replicate dialysis samplers may vary because samples are collected at different times after removal from the well. Samples should be collected as soon as possible after the dialysis sampler has been removed from the well. Sampling one dialysis sampler immediately after removal from a well while waiting for 30 minutes to sample another that has been exposed to the atmosphere may result in chemical differences particularly if volatile or redox active constituents are being collected.

7.0 SUMMARY

7.1 Situational Use of Dialysis Samplers

Dialysis samplers may be used in any well where ground water passes freely through the screened or open interval. Dialysis samplers may be used in most wells where low-flow purging methods are currently used. The use of dialysis samplers may be particularly advantageous over low-flow purging to sample wells in the following situations:

- Wells that are located in areas where it would be difficult or impossible to bring in a pump and its power source, (wells in remote wilderness areas, wells inside buildings),
- Wells that are located in areas where normal sampling activities would be extremely hazardous or inconvenient, (wells in high traffic areas, wells in airport runway areas),
- Wells located in areas where a low profile would be desirable, (residential areas near military bases),
- Wells located in areas where collection, transport, and treatment of purge water would be costly, difficult, or undesirable due to safety concerns, (wells at all hazardous waste sites, wells at remote hazardous waste sites, wells in populated areas near military bases),
- Wells that have high turbidity when purged due to their construction or the formation they are completed in, (incorrect screen size or filter pack), and
- Sites with large numbers of wells for long-term monitoring of both inorganics and VOC.

Dialysis samplers should not be used in the following situations:

- Wells where whole water samples must be collected,
- Wells where a large sample volume (>3-4 liters) is required, or
- Wells that must be sampled for mercury, silver, and tin.

7.2 Approved Regulatory Use of Dialysis Samplers

One example of regulatory approval being granted for the use of dialysis samplers to replace low-flow purging is the NAWC, West Trenton, NJ site (Imbrigiotta et al., 2002; Imbrigiotta et al. 2007). After two rounds of side-by-side comparisons, the NJ Department of Environmental Protection approved the routine use of dialysis samplers in 25 wells in the long-term monitoring plan at the NAWC, West Trenton, NJ site. The U.S. Navy contractor saves time in the field by not having to purge these 25 wells to collect samples, by not having to decontaminate pumps between these wells, and by not having to collect, transport, and treat purge water from these wells. As a result, the U.S. Navy is saving a significant amount of funding in its annual long-term monitoring program at this site.

7.3 Conclusions

The following conclusions can be made regarding the protocols for use of regenerated-cellulose dialysis samplers based on the results of the work in ESTCP project ER-0313 (Imbrigiotta et al., 2007) and the other laboratory and field studies reviewed in the literature:

- Dialysis samplers can collect valid groundwater samples for most inorganic and organic constituents that compare favorably to samples collected by low-flow purging and other conventional purging methodologies.

- The length of time dialysis samplers should be deployed in the well prior to recovery depends on the equilibration time for the chemical constituents of interest and the time required for restabilization of the groundwater flow field through the open interval of the well. Laboratory equilibration testing and field comparison data suggest that one to two week deployment times are sufficient for most inorganic and organic constituents. Slightly longer deployment times may be necessary for equilibration of explosive compounds. In less permeable formations, longer restabilization times may be required.

- A dialysis sampler should be placed at the depth where the highest mass flux of the chemical of concern passes through the screened or open interval of each well. This means the variation in groundwater flow and any stratification of concentrations of chemicals of interest should be determined over the length of the screened or open interval prior to the first deployment of a dialysis sampler. Vertical profiling by both hydraulic and chemical methods should be conducted to obtain this information.

- For open intervals 5 feet or less in length, chemical and hydraulic vertical profiling is usually not necessary. For open intervals 5 feet or greater, chemical and vertical profiling should be conducted. Chemical profiling may be done by equilibrating dialysis samplers at closely spaced intervals (2-5 ft) over the length of the open interval of a well and analyzing them for a parameter indicative of the contamination. Hydraulic profiling may be done using a borehole flow meter or straddle-packer pump setup.

- The size of a dialysis sampler should be the shortest of the following lengths depending on the individual well: 5 feet in length, the length of the well screen, the length of the zone of highest mass influx of the contaminants of concern, or the length that will contain the minimum amount of water needed for the chemicals being analyzed.

- Side-by-side comparisons of dialysis samplers with other sampling technologies may be necessary to establish the applicability of dialysis samplers. In wells where there has historically been little variation in contaminant concentration and groundwater elevation, comparison of dialysis sampler results to the historical record may provide enough information to determine whether dialysis samplers are appropriate for the wells.

- Re-profiling wells or changing the vertical location of an established dialysis sampler monitoring point should not be necessary unless there is evidence to suggest that the

contaminant distribution, well hydraulics, or well characteristics have changed since the initial vertical profiling was conducted.

- Deoxygenated deionized water should be used to fill and store dialysis samplers that will be deployed in anoxic wells to avoid altering the concentrations of redox active chemicals.

- Dialysis samplers can easily be deployed by one person and sampled by two persons. The basic considerations in deploying diffusion samplers include that they must be installed below the air/water interface in a well and they must remain submerged and be allowed to equilibrate for the appropriate period of time for the chemicals of concern at a site.

- Dialysis samplers made with regenerated-cellulose dialysis membrane must be kept hydrated between the time of construction and deployment.

- Dialysis sampler limitations due to water volume loss with time and biodegradation are minimized when deployment times in wells are one to two weeks.

- Dialysis samplers may recover contaminant concentrations higher or lower than those recovered by other sample collection methods for several reasons including, field comparison test design, well construction, differences between sampling mechanisms, acceptance criteria agreed upon with regulators, and the influence of chemical stratification and hydraulic heterogeneity.

- It is essential that all parties involved in the use of dialysis samplers at regulated sites must identify and agree on the objectives of data collection, data evaluation techniques, and data end uses before dialysis sampler deployment takes place.

- No regulatory issues have been identified that would restrict the application of dialysis samplers in technically appropriate situations.

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